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Process for the Production of Formic Acid Alkyl Esters

[Verfahren zur Herstellung von Ameisensaurealkylestern]

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Patent 863 046 describes a particularly advantageous process for the production of formic acid alkyl esters. This process involves the following: one so-selects the reaction condition, especially the pressure and the temperature that at least so much of the aliphatic alcohol will remain unchanged that the middle alkylates which are used as catalysts will be kept dissolved and the carbon monoxide, with a partial pressure of up to 30 atm abs and the alkylate solution will be mixed with each other, in a countercurrent where the formed formic acid esters will be removed from the carbon monoxide present in excess out of the reaction zone, while the catalyst solution is continually conducted in a special circuit and the process is renewed.

It was now found that one can achieve considerably better results by proceeding in the following manner: one continually so introduces into the mixing zone between carbon monoxide or carbon monoxide containing gases as well as the pertinent aliphatic alcohols, such as methanol that contain alkaline metals, alkaline earth metals or their alcoholates in solution that both the alkylate solution as well as the carbon monoxide will in the identical current specially in the direction from underneath toward the top, flow through the reaction vessel. As

¹ Numbers in the margin indication pagination in the foreign text.

such, one should have expected the opposite because, in the case at hand, the countercurrent would also be advantageous because in that way, one would expect better reaction conditions. 2 Extensive experiments however showed that by proceeding in this manner, one can practically avoid any possible diminution of the mixing and disturbances of continual operations such as they happen in the past, if one works according to the new procedure. As for the rest, one proceeds in the same manner as described in the patent 863 046.

Example

The reaction tower 1 illustrated in a form of a diagram in the figure, is used for the continue production of methyl formiate. It consisted of an 8 meter long pressure resistant iron pipe with an inside clearance of 35 cm and was charged with iron filler body rings. The upper end of the reaction tower emptied into a 45 cm high steam dome 2 with an inside clearance of 18.5 cm. Two suction glasses were attached to the steam dome and they made it possible to keep the liquid level at a certain height. Methanol, sodium ethylate and carbon monoxide were pumped into the lower part of the reaction tower 1 that by the way, was well insulated against heat transfer, just as was the steam dome. The sodium ethylate as one can see in the drawing is made in a stirring mechanism tank 3 from methanol and metallic sodium and was conveyed into the reaction tower via the

methyrate pump 4. The methanol flowed out of tank 5 to the methanol pump 6 and was conveyed by the latter, via the methanol pre-heater 7 at a temperature of 85-90°, into the reaction tower.

Furthermore, all of the liquid present in the reaction tower was so turned over by means of the liquid revolution pump 8 at a speed of 15 liters/hour, that the liquid stream was conducted from underneath toward the top, through the reaction tower.

In the same direction of flow as the liquid, carbon monoxide, coming from the gas revolution pump 9, was conducted through carbon monoxide pre-heater 10 with a speed of 17 m³/hour at 0° with 76° mm into the reaction tower.

The input temperature of the carbon monoxide into the reaction tower was so adjusted with the electrically heated pre-heater 10 that after through mixing of gas and liquid, one obtained a temperature of 85 - 88° something that was the case in the reaction chamber approximately at a height of 0.80 to 1.20 meter. During the experiments that were performed, the temperature was constant through out the entire length of the reaction tower, that is to say, the heat evacuation toward the environment was compensated by the heat generated by the reaction.

The dried fresh carbon monoxide was compressed in the compressor 11, and with the help of the automatically working pressure regulator 12, so much was supplied to the gas cycle as was consumed by the formation of methyl formate carbon monoxide [sic.] in the reaction tower.

Together with the circulating gas, the methyl formate and a portion of methanol corresponding to its partial pressure emerged at the upper end of the steam dome 2. After passing through the cooler 13, the gas was separated from the liquid in the pressure separator 14. The former [gas] was returned to the gas circulating pump 9, while the liquid consisting of methyl formate and methanol was released to normal pressure by means of the valve attached between 14 and the pressure release tank 15.

When one uses pure carbon monoxide and when one works at a working pressure of 30 atm abs then it was possible in the arrangement described above, to produce 3.1 kg of methyl formate per hour during sustained operation. The methyl formate was obtained with a methanol content of 38-40%.

In two additional attempts we used in place of pure carbon monoxide gas, a mixture that consisted of 50% hydrogen and 50% carbon monoxide. The output of the reaction tower at 50% atm abs amounted to a total pressure of 2.6 kg methyl formate per hour with a content of 38% methanol and when we used 30 atm abs,

we got 2.1 kg of methyl formiate per hour with a content of 45% methanol. To separate the methyl formiate from the methanol we allowed the liquid mixture to run into the plate column 16 and methyl formiate was taken out at the head of same. The unmixed methanol that was also introduced out of the reaction tower was taken out in the form of steam at the lower end of the column, it was condense in the cooler 17 and it was supplied to the methanol tank 5 from where it was piped into the cycle supplemented with fresh methanol. Unfortunately, one cannot prevent the formation of small quantities of sodium formiate in the reaction tower. To make sure that this sodium formiate was not enriched, a part of the circulating liquid was continually taken out and the dosage of the fresh catalyst was adjusted accordingly.

A catalyst concentration of 1.6 to 2.5% sodium related to the circulating liquid proved effective in the experiments that were performed. Higher catalyst concentrations can also be employed successfully.

CLAIMS

Development of the process described in patent 863 046 for the production of formic acid alkyl esters by mixing carbon monoxide with aliphatic alcohols in the presence of alkali or alkaline earth metals or their alkoxy compounds dispensing with the complete mixing of the existing alcohol during continual

operation, whereby the alcoholate remains dissolves in the alcohol that has not changed and the reaction conditions especially the pressure and the temperature are so selected that at least so much of the aliphatic alcohol will remain unchanged that the alkylates used as catalyst will remain dissolved and that the catalyst solution and the carbon monoxide will continually be moved in a special cycle and here possibly the catalyst solution will be partly renewed characterized in that both the carbon monoxide and the alkylate catalyst solution will be conducted in an identical current from underneath toward the top, through the mixing vessel.

